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VERIFICATION OF TRANSLATION

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Sir:

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declares:

1) that I know well both the Japanese and English languages;

2) that I translated the priority document of the Japanese Patent Application No. 2003-295269 from Japanese to English;

3) that the attached English translation is a true and accurate translation of the priority document of the Japanese Patent Application No. 2003-295269 to the best of my knowledge and belief; and

4) that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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【Document Name】 Claims

【Claim 1】

A substrate processing method comprising:

a first step of supplying an alkaline processing solution to a substrate;

a second step of supplying an acid processing solution to the substrate after said first step; and

a third step of supplying an alkaline processing solution to the substrate after said second step,

wherein at least either the supply of the processing solution in said second step or the supply of the processing solution in said third step is either an injection of droplets generated by mixing the processing solution with a gas, or a supply of the processing solution with ultrasonic vibrations imparted thereto.

【Claim 2】

The substrate processing method according to claim 1, wherein

out of said three steps, only the supplies of the alkaline processing solution in said first and third steps are either injections of droplets generated by mixing the processing solution with a gas, or supplies of the processing solution with ultrasonic vibrations imparted thereto.

【Claim 3】

The substrate processing method according to either claim 1 or 2, wherein

said alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【Claim 4】

The substrate processing method according to any one of claims 1 to 3, wherein

said acid processing solution is a mixed solution containing hydrochloric acid

and hydrofluoric acid.

【Claim 5】

A substrate processing method comprising:

a first step of supplying an alkaline processing solution to a substrate; and

a second step of, after said first step, repeating a supply of an acid processing solution and the following supply of an alkaline processing solution to the substrate,

wherein at least one supply of the processing solution in said second step is either an injection of droplets generated by mixing the processing solution with a gas, or a supply of the processing solution with ultrasonic vibrations imparted thereto.

【Claim 6】

The substrate processing method according to claim 5, wherein

said alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【Claim 7】

The substrate processing method according to either claim 5 or 6, wherein

said acid processing solution is a mixed solution containing hydrochloric acid and hydrofluoric acid.

【Claim 8】

A substrate processing apparatus performing given processing on a substrate, the apparatus comprising:

a first supply means for supplying an alkaline processing solution to a substrate;

a second supply means for supplying an acid processing solution to the substrate;

a control means for controlling said first supply means and said second supply means so as to perform, in sequence, the supply of the alkaline processing solution with

said first supply means, the supply of the acid processing solution with said second supply means, and the supply of the alkaline processing solution with said first supply means,

wherein at least either said first supply means or said second supply means includes a binary fluid nozzle that injects droplets of the alkaline processing solution, or an ultrasonic nozzle that supplies the alkaline processing solution with ultrasonic vibrations imparted thereto.

【Claim 9】

The substrate processing apparatus according to claim 8, wherein

out of said first supply means and said second supply means, only said first supply means includes a binary fluid nozzle that injects droplets of the alkaline processing solution, or an ultrasonic nozzle that supplies the alkaline processing solution with ultrasonic vibrations imparted thereto.

【Claim 10】

The substrate processing apparatus according to either claim 8 or 9, wherein

said alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【Claim 11】

The substrate processing apparatus according to any one of claims 8 to 10, wherein

said acid processing solution is a mixed solution containing hydrochloric acid and hydrofluoric acid.

【Document Name】 Specification

【Title of the Invention】 SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

【Technical Field of the Invention】

【0001】

The present invention relates to a substrate processing method and a substrate processing apparatus, both for cleaning surfaces of substrates such as semiconductor wafers, glass substrates for liquid crystal displays, glass substrates for photomasks, and substrates for optical disks.

【Background Art】

【0002】

For example in various stages in the process of manufacturing a semiconductor device, fine particles and various metal contaminants adhere to a semiconductor-wafer surface. It is thus necessary to clean the wafer surface to remove those particles and metal contaminants from the substrate surface. A batch method is conventionally employed as a wafer cleaning method, in which a number of wafers are dipped into a cleaning solution at a time to be cleaned. Cleaning solutions used herein include chemical solutions such as a mixed solution of ammonia water and a hydrogen peroxide solution and a mixed solution of hydrochloric acid and a hydrogen peroxide solution, and also include, depending on the purpose, a combination of those chemical solutions and other chemical solutions such as hydrofluoric acid. Although requiring a long processing time per lot, this batch immersion and cleaning method ensures a certain level of productivity because of its simultaneous processing of a number of wafers.

【0003】

With various processing advantages in view, on the other hand, a single-wafer

cleaning method is also employed, in which, with a wafer kept in a horizontal position and rotated about a vertical axis one by one, a cleaning solution is supplied to the substrate surface for cleaning. A major issue with this single-wafer cleaning method is productivity, and how to shorten the processing time per wafer is an important problem. To meet this need, various cleaning processes suitable for the single-wafer cleaning method are now developed. For instance, one process is suggested which uses a combination of ozone water and dilute hydrofluoric acid as a cleaning solution, thereby to improve decontamination performance and to shorten the processing time. According to this process, ozone water is first supplied to a wafer surface for oxidization of the wafer surface, and then dilute hydrofluoric acid is supplied to the wafer surface for selective etching of only an oxide layer in the wafer surface. This results in removal of metal contaminants adhering to the wafer surface as well as the oxide layer from the wafer surface. Eliminating the particle-holding layer from the wafer surface also results in removal of particles (see, for example, Patent Document 1).

【0004】

【Patent Document 1】 Japanese Patent Application Laid-open No. 10-256211 (pp. 2-3)

【Disclosure of the Invention】

【Problems to be Solved by the Invention】

【0005】

The aforementioned process that uses a combination of ozone water and dilute hydrofluoric acid as a cleaning solution, however, has a problem on the effect of particle removal, because ozone water itself has no ability to remove particles. The above process also has another problem that the use of hydrofluoric acid for removal of metal contaminants and particles from the wafer surface requires deep etching of the layer of

the wafer surface and thus increases the amount of etching of the wafer surface.

【0006】

The present invention has been made in view of the aforementioned circumstances, and aims to provide a substrate processing method that allows, for substrate cleaning on a single-wafer basis, effective and short-time removal of particles and metal contaminants from a substrate surface without any increase in the amount of etching of the substrate surface; and also aims to provide a substrate processing apparatus that is capable of suitably implementing that method.

【Means for Solving the Problems】

【0007】

A first aspect of the invention is directed to a substrate processing method including: a first step of supplying an alkaline processing solution to a substrate; a second step of supplying an acid processing solution to the substrate after the first step; and a third step of supplying an alkaline processing solution to the substrate after the second step, wherein at least either the supply of the processing solution in the second step or the supply of the processing solution in the third step is either an injection of droplets generated by mixing the processing solution with a gas, or a supply of the processing solution with ultrasonic vibrations imparted thereto.

【0008】

According to a second aspect of the invention, in the substrate processing method according to the first aspect, out of the three steps, only the supplies of the alkaline processing solution in the first and third steps are either injections of droplets generated by mixing the processing solution with a gas, or supplies of the processing solution with ultrasonic vibrations imparted thereto.

【0009】

According to a third aspect of the invention, in the substrate processing method according to either the first or second aspect, the alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【0010】

According to a fourth aspect of the invention, in the substrate processing method according to any one of the first to third aspects, the acid processing solution is a mixed solution containing hydrochloric acid and hydrofluoric acid.

【0011】

A fifth aspect of the invention is directed to a substrate processing method including: a first step of supplying an alkaline processing solution to a substrate; and a second step of, after the first step, repeating a supply of an acid processing solution and the following supply of an alkaline processing solution to the substrate, wherein at least one supply of the processing solution in the second step is either an injection of droplets generated by mixing the processing solution with a gas, or a supply of the processing solution with ultrasonic vibrations imparted thereto.

【0012】

According to a sixth aspect of the invention, in the substrate processing method according to the fifth aspect, the alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【0013】

According to a seventh aspect of the invention, in the substrate processing method according to either the fifth or sixth aspect, the acid processing solution is a mixed solution containing hydrochloric acid and hydrofluoric acid.

【0014】

An eighth aspect of the invention is directed to a substrate processing apparatus

performing given processing on a substrate, the apparatus including: a first supply means for supplying an alkaline processing solution to a substrate; a second supply means for supplying an acid processing solution to the substrate; a control means for controlling the first supply means and the second supply means so as to perform, in sequence, the supply of the alkaline processing solution with the first supply means, the supply of the acid processing solution with the second supply means, and the supply of the alkaline processing solution with the first supply means, wherein at least either the first supply means or the second supply means includes a binary fluid nozzle that injects droplets of the alkaline processing solution, or an ultrasonic nozzle that supplies the alkaline processing solution with ultrasonic vibrations imparted thereto.

【0015】

According to a ninth aspect of the invention, in the substrate processing apparatus according to the eighth aspect, out of the first supply means and the second supply means, only the first supply means includes a binary fluid nozzle that injects droplets of the alkaline processing solution, or an ultrasonic nozzle that supplies the alkaline processing solution with ultrasonic vibrations imparted thereto.

【0016】

According to a tenth aspect of the invention, in the substrate processing apparatus according to either the eighth or ninth aspect, the alkaline processing solution is a mixed solution containing ammonia water and a hydrogen peroxide solution.

【0017】

According to an eleventh aspect of the invention, in the substrate processing apparatus according to any one of the eighth to tenth aspects, the acid processing solution is a mixed solution containing hydrochloric acid and hydrofluoric acid.

【Advantageous Effect of the Invention】

【0018】

According to the first to eleventh aspects of the invention, effective and short-time removal of particles adhering to a substrate surface is possible by the combined use of etching of the substrate surface with the acid processing solution and physical action of the droplet injection or the ultrasonic vibrations. Metal contaminants adhering to the substrate surface, on the other hand, can also be removed effectively in a short time because they are dissolved in the acid processing solution after converted into hydroxides with the alkaline processing solution. It is also possible to minimize the amount of etching of the substrate surface, unlike in the case where particles and metal contaminants are removed mainly by etching of the substrate surface.

【0019】

In particular, according to the second to ninth aspects of the invention, after most particles on the substrate surface are removed beforehand by the injection of droplets of the alkaline processing solution, remaining particles on the substrate surface are removed by the combined use of etching of the substrate surface with the acid processing solution and physical action of the droplet injection or the ultrasonic vibrations. This further improves the effectiveness of particle removal.

【0020】

In particular, according to the third, sixth, and tenth aspects of the invention, since the alkaline processing solution is mixed with a hydrogen peroxide solution as an oxidizing agent, it is possible to protect the surface of a wafer W to be processed.

【Best Mode for Carrying out the Invention】

【0021】

A preferred embodiment of the present invention is now described with reference to the drawings.

【0022】

Figs. 1 to 3 show, by way of example, a structure of a substrate processing apparatus for use in implementing a substrate processing method according to the present invention: Fig. 1 is a plan view of the apparatus; Fig. 2 is a schematic end view of the essential parts of the apparatus when viewed in the direction of the arrow A in Fig. 1; and Fig. 3 is another schematic end view of the essential parts of the apparatus when viewed in the direction of the arrow B in Fig. 1. For clarity, Fig. 2 does not show a mechanism for supplying an acid processing solution; and Fig. 3 does not show a mechanism for supplying an alkaline processing solution.

【0023】

This substrate processing apparatus includes a disc-shaped spin base 10 that supports a substrate, e.g., a semiconductor wafer W, in a horizontal position. On the upper peripheral edge of the spin base 10, a plurality of, e.g., six, chuck pins 12 are circumferentially arranged at regular intervals to grasp the peripheral edge of the wafer W. The chuck pins 12 each have a support part 12a that is in engagement with the lower peripheral edge of the wafer W to support the wafer W; and a fixing part 12b that fixes the wafer W by pressing the outer peripheral end face of the wafer W held on the support part 12a. Although its detailed structure is not shown, the fixing parts 12b of the chuck pins 12 are switchable between the state of pressing the outer peripheral end face of the wafer W for fixation of the wafer W and the state of leaving the outer peripheral end face of the wafer W for a release of the wafer W.

【0024】

The spin base 10 has a through hole 14 formed in the central portion, and a cylindrical rotary spindle 16 is suspended from the underside of the spin base 10 to communicate with the through hole 14. Around the cylindrical rotary spindle 16, there

is a lidded cylindrical casing 20 fixed on a base plate 18. The cylindrical rotary spindle 16 is supported by the base plate 18 and the casing 20 so as to be rotatable about a vertical axis through bearings 22 and 24. In the casing 20, a motor 26 is arranged and fixed on the base plate 18. A drive-side pulley 28 is fixed to the rotary shaft of the motor 26, while a driven-side pulley 30 is fitted for attachment to the cylindrical rotary spindle 16, with a belt 32 looped over the drive-side pulley 28 and the driven-side pulley 30. This mechanism causes the cylindrical rotary spindle 16 to rotate and in turn causes the wafer W, which is held on the spin base 10 fixed to the upper end of the cylindrical rotary spindle 16, to rotate in a horizontal plane. A nozzle 34 channel-connected to a cleaning-solution supply source is inserted into a hollow portion of the cylindrical rotary spindle 16. This nozzle 34 discharges a cleaning solution from its upper discharge port toward the central portion of the underside of the wafer W held on the spin base 10.

【0025】

Around the casing 20, a cylindrical wall part 36 arranged to surround the casing and a bottom wall part 38 formed integrally with this cylindrical wall part 36 and in connection with the lower end of the cylindrical outer peripheral surface of the casing 20 are arranged and fixed on the base plate 18. The cylindrical portion of the casing 20, the cylindrical wall part 36, and the bottom wall part 38 form a recovery tank 40. The bottom wall part 38, which is the bottom of the recovery tank 40, has a V-shaped longitudinal section and has a discharge hole 42 formed therein. The base plate 18 has a discharge port 44 formed therein to provide a communication with the discharge hole 42. Although not shown, the discharge port 44 is openly connected with a recovery pipe that is channel-connected to a tank for collection of a cleaning solution or the like.

【0026】

Beside one side of the cylindrical wall part 36, as shown in Fig. 2, a mechanism

46 for supplying an alkaline processing solution that is a mixed solution of ammonia water, a hydrogen peroxide solution, and pure water is provided. The alkaline-processing-solution supply mechanism 46 includes a binary fluid nozzle 48 having a discharge port arranged above the wafer W held on the spin base 10 to face the surface of the wafer W. The binary fluid nozzle 48 is fixed to the tip of an arm 50, so that the arm 50 is kept in a horizontal position by an arm holding part 52 in a cantilever manner. The arm holding part 52 is fixed to the top of a vertically-arranged rotary spindle 54. The rotary spindle 54 is coupled to a nozzle moving mechanism 56 and is caused by the nozzle moving mechanism 56 to rotate and to reciprocate vertically. Driving the nozzle moving mechanism 56 causes the binary fluid nozzle 48 to swing in a horizontal plane and to reciprocate between the central and peripheral portions of the wafer W, and it also causes the binary fluid nozzle 48 to approach or leave the surface of the wafer W. The arm 50 holding the binary fluid nozzle 48 , as shown by two-dot chain lines in Fig. 1, is capable of retracting into a position outside the cylindrical wall part 36. The nozzle moving mechanism is not limited to the one illustrated, and it may be any one of various mechanisms.

【0027】

The binary fluid nozzle 48, as shown in a longitudinal sectional view of Fig. 4, includes a tubular liquid supply nozzle part 58 having a through hole 60 in the axial center; and a cylindrical gas supply nozzle part 62 integrally fixed to the nozzle part 58 to surround the outer periphery of the nozzle part 58 and having an annular hole 64 formed between its concave stepped surface, which is its lower-half inner peripheral surface, and a lower-half outer peripheral surface of the liquid supply nozzle part 58. A discharge port of the liquid supply nozzle part 58 and an annular discharge port of the gas supply nozzle part 62 are in a concentric arrangement. The annular hole 64 in the gas supply

nozzle part 62 is tapered toward the discharge port so as to be oriented to a point on an extension line of the through hole 60 in the liquid supply nozzle part 58. Further, the lower end of the gas supply nozzle part 62 extends annularly downward below the lower end of the liquid supply nozzle part 58 to define a largely and externally opened injection port 66 that faces the discharge port of the liquid supply nozzle part 58 and the annular discharge port of the gas supply nozzle part 62.

【0028】

The through hole 60 in the liquid supply nozzle part 58 is openly connected to an alkaline-processing-solution supply pipe 68 that is channel-connected to a supply source (not shown) of an alkaline processing solution which is a mixed solution of ammonia water, a hydrogen peroxide solution, and pure water. The alkaline-processing-solution supply pipe 68 has an on-off control valve 70 inserted therein. The gas supply nozzle part 62 has an air introduction tube 72 arranged to communicate with the annular hole 64, and the air introduction tube 72 is openly connected to an air supply pipe 74 that is channel-connected to a compressed-air source (not shown). The air supply pipe 74 has an on-off control valve 76 inserted therein.

【0029】

In the binary fluid nozzle 48 with the above-described structure, when the on-off control valve 70 is opened to supply an alkaline processing solution (a mixed solution of ammonia water, a hydrogen peroxide solution, and pure water) from the alkaline-processing-solution supply source through the alkaline-processing-solution supply pipe 68 to the liquid supply nozzle part 58, the liquid supply nozzle part 58 discharges the alkaline processing solution directly downwardly from its lower-end discharge port. When the on-off control valve 76 is opened to feed compressed air from the compressed-air source through the air supply pipe 74 to the air introduction tube 72,

on the other hand, the gas supply nozzle part 62 discharges the compressed air from its annular discharge port through the annular hole 64. The compressed air discharged from the annular discharge port of the gas supply nozzle part 62 goes to converge on a point on the extension line of the through hole 60 in the liquid supply nozzle part 58, thus colliding with the alkaline processing solution that moves straight downward from the lower-end discharge port of the liquid supply nozzle part 58. This generates droplets that are a mixture of the alkaline processing solution and the compressed air. The droplets 77, issuing from the injection port 66 while slightly spreading in a conical form, are injected onto the surface of the wafer W.

【0030】

Beside another side of the cylindrical wall part 36, as shown in Fig. 3, a mechanism 78 for supplying an acid processing solution that is a mixed solution of hydrofluoric acid, hydrochloric acid, and pure water is provided. The acid-processing-solution supply mechanism 78 includes a nozzle 80 having a discharge port arranged above the wafer W held on the spin base 10 to face the surface of the wafer W. The nozzle 80 is fixed to the tip of an arm 82 that is kept in a horizontal position by an arm holding part 84 in a cantilever manner. The arm holding part 84 is fixed to the top of a vertically-arranged rotary spindle 86. The rotary spindle 86 is coupled to a nozzle moving mechanism 88 and is caused by the nozzle moving mechanism 88 to rotate and to reciprocate vertically. Driving the nozzle moving mechanism 88 causes the nozzle 80 to swing in a horizontal plane and to reciprocate between the central and peripheral portions of the wafer W, and also causes the nozzle 80 to approach or leave the surface of the wafer W. The arm 82 holding the nozzle 80 is capable of retracting into a position outside the cylindrical wall part 36 by rotation from the position shown by the two-dot chain lines in Fig. 1 to the position shown by the solid lines. The nozzle moving

mechanism is not limited to the one illustrated, and it may be any one of various mechanisms.

【0031】

The nozzle 80 is openly connected with a liquid supply pipe 110 for supplying an acid processing solution or the like. The liquid supply pipe 110 is channel-connected to an acid-processing-solution supply source (not shown) through an on-off control valve 115. The liquid supply pipe 110 is also channel-connected to a pure-water supply source through an on-off control valve 117, so that it is capable of selectively supplying either an acid processing solution or pure water by on-off control of the on-off control valves 115 and 117.

【0032】

This substrate processing apparatus further includes, in addition to the components described above, a control part 91 that controls the operations of the motor 26, the nozzle moving mechanisms 56 and 88, the on-off control valves 70, 76, 115, and 117, and the like.

【0033】

Next, a method for cleaning the wafer W with the substrate processing apparatus with the aforementioned structure is described by way of example. Fig. 5 shows, by way of example, the steps in the process of cleaning the wafer W. As shown in Fig. 5, the process of cleaning the wafer W according to the present preferred embodiment is performed in the following order: introduction of the wafer W (step S1); a droplet injection of an alkaline processing solution (step S2); a supply of an acid processing solution (step S3); a droplet injection of the alkaline processing solution (step S4); rising (step S5); spin drying (step S6); and discharge of the wafer W (step S7). These steps in the cleaning process are carried out by the aforementioned control part 91

controlling the operations of the motor 26, the nozzle moving mechanisms 56 and 88, the on-off control valves 70, 76, 115, and 117, and the like.

【0034】

In step S1, first, with both the binary fluid nozzle 48 and the nozzle 80 in their retracted positions outside the cylindrical wall part 36, a pre-cleaned wafer W is transported onto the spin base 10 with a transport robot (not shown) and then fixed thereto by its outer peripheral end face being pressed with the plurality of chuck pins 12.

【0035】

In step S2, the motor 26 is driven to rotate the wafer W on the spin base 10 in a horizontal plane. The nozzle moving mechanism 56 is also driven to cause the binary fluid nozzle 48 to approach the surface of the wafer W and then to swing in a horizontal plane. The binary fluid nozzle 48 then injects the droplets 77 of the alkaline processing solution (the mixed solution of ammonia water, a hydrogen peroxide solution, and pure water) to the surface of the wafer W, while reciprocating between the central and peripheral portions of the wafer W along the surface of the wafer W on the spin base 10. This shall be done at ordinary temperatures without controlling the temperature of the alkaline processing solution. At the same time, a cleaning solution such as pure water is also discharged from the upper-end discharge port of the nozzle 34 toward the central portion of the underside of the wafer W held on the spin base 10. This discharge of pure water or the like to the central portion of the underside of the wafer W may be performed afterward as necessary.

【0036】

In this step S2, since the droplets injected from the binary fluid nozzle 48 collide with the surface of the wafer W, particles adhering to the surface of the wafer W are physically removed with the kinetic energy of the droplets. Since the alkaline

processing solution injected onto the surface of the wafer is in the form of droplets and thus does not give an excessive impact on the wafer itself, even if an electronic circuit pattern is on the surface of the wafer W, that pattern is not damaged.

【0037】

Potentials (zeta potential) on the surface of major particles such as PSL (polystyrene latex), Si_3N_4, SiO_2, and Si are negatively charged in an alkaline aqueous solution, whereas the zeta potential on the surface of the wafer (silicon wafer) W in contact with the alkaline aqueous solution is also negatively charged. In this case, since the zeta potentials on the surface of the wafer W and on the surfaces of the particles are of the same polarity, repulsion is produced between the wafer W and the particles. This repulsion caused by the zeta potentials prevents re-deposition of particles that liberated from the surface of the wafer W, thereby providing efficient particle removal.

【0038】

Also in this step S2, the supply of the alkaline processing solution causes metal contaminants, such as Fe and Cu, adhering to the surface of the wafer W to be converted into hydroxides. This facilitates dissolution of the metal contaminants in the next step S3.

【0039】

In step S3, after the binary fluid nozzle 48 is alienated from the surface of the wafer W and retracted into a position outside the cylindrical wall part 36 as shown by the two-dot chain lines in Fig. 1, the nozzle moving mechanism 88 is driven to move the nozzle 80 from its retracted position shown by the solid lines in Fig. 1 to the position above the wafer W shown by the two-dot chain lines. The nozzle 80 is then driven to approach the surface of the wafer W and to swing in a horizontal plane, thereby to supply droplets of an acid processing solution (a mixed solution of hydrofluoric acid,

hydrochloric acid, and pure water) to the surface of the wafer W, while reciprocating between the central and peripheral portions of the wafer W along the surface of the wafer W on the rotating spin base 10. This shall be done at ordinary temperatures without controlling the temperature of the acid processing solution.

【0040】

In this step S3, the supply of the acid processing solution to the wafer W results in dissolution (ionization) and removal of metal contaminants adhering to the surface of the wafer W. Here, the previous conversion of the metal contaminants adhering to the surface of the wafer W into hydroxides in step S2 increases the speed of dissolution in the acid processing solution in step S3. Such speedy processing minimizes the amount of surface etching of the wafer W with the acid processing solution in removing metal contaminants.

【0041】

In step S4, after the nozzle 80 is alienated from the surface of the wafer W and retracted into a position outside the cylindrical wall part 36 as shown by the solid lines in Fig. 1, the nozzle moving mechanism 56 is driven to move the binary fluid nozzle 48 from its retracted position shown by the two-dot chain lines in Fig. 1 to the position above the wafer W shown by the solid lines. The binary fluid nozzle 48 is then driven to approach the surface of the wafer W and to swing in a horizontal plane, thereby to inject the droplets 77 of the alkaline processing solution (the mixed solution of ammonia water, a hydrogen peroxide solution, and pure water) to the surface of the wafer W, while reciprocating between the central and peripheral portions of the wafer W along the surface of the wafer W on the rotating spin base 10.

【0042】

Although most particles are removed in step S2, some particles may remain on

the surface of the wafer W without been removed in step S2, for example when particles are embedded in the surface of the wafer W or when they are strongly adsorbed on the surface of the wafer W and thus hard to remove. These particles come to the surface of the wafer W and are brought into an easy-to-remove condition when the surface of the wafer is slightly etched with the supply of the acid processing solution in step S3. In this step S4, such particles are removed by an injection of the droplets 77 of the alkaline processing solution to the surface of the wafer W.

【0043】

In this step S4, as in step S2, particles adhering to the surface of the wafer W are physically removed with the kinetic energy of droplets. Besides, repulsion caused by the zeta potentials in the alkaline processing solution prevents re-deposition of particles once liberated from the surface of the wafer W, thereby providing efficient particle removal.

【0044】

In order for such particles to come to the surface and be removed by only etching with the acid processing solution, the amount of surface etching of the wafer W has to be increased; however, since the present embodiment suggests the combined use of etching with the acid processing solution and the physical action resulting from the droplet injection, it is possible to remove such particles while minimizing the amount of surface etching of the wafer W.

【0045】

In step S5, after the binary fluid nozzle 48 is alienated from the surface of the wafer W and retracted into a position outside the cylindrical wall part 36 as shown by the two-dot chain lines in Fig. 1, the nozzle moving mechanism 88 is driven to move the nozzle 80 from its retracted position shown by the solid lines in Fig. 1 to the position

above the wafer W shown by the two-dot chain lines. The nozzle 80 is then driven to approach the surface of the wafer W and to swing in the horizontal plane, thereby to discharge pure water to the surface of the wafer W for rinsing, while reciprocating between the central and peripheral portions of the wafer W along the surface of the wafer W on the rotating spin base 10. Alternatively, another discharge nozzle exclusively for use in discharging pure water may be provided aside from the nozzle 80, and pure water may be discharged from that discharge nozzle to the surface of the wafer W.

【0046】

In step S6, the rotational frequency of the motor 26 is increased to rotate the wafer W at high speed and thereby to drain moisture adhering to the surface of the wafer W for drying (spin-drying). After the completion of the drying of the surface of the wafer W, the motor 26 is stopped to stop the rotation of the wafer W.

【0047】

In step S7, with both the binary fluid nozzle 48 and the nozzle 80 in their retracted positions outside the cylindrical wall part 36, the plurality of chuck pins 12 that fix the wafer W by pressing the outer peripheral end face of the wafer W are released, and the wafer W on the spin base 10 is transported out of the apparatus with the transport robot (not shown). This completes the process of cleaning a single wafer W.

【0048】

In the aforementioned sequence of the process steps, the alkaline processing solution and the acid processing solution may be at ordinary temperatures (in the range of 20 to 30°C). If the room temperature is kept at ordinary temperatures, both the alkaline and acid processing solutions can be used without any particular necessity of controlling the liquid temperatures. This simplifies the processing of the wafer W. In other word, since the time and equipment required for temperature control before and after processing

are unnecessary, it is possible to shorten the processing time and to reduce the cost. Further, performing the processing at ordinary temperatures results in a marked reduction in the amount of etching of the wafer W with the alkaline and acid processing solutions, as compared to performing processing at high temperatures (about 65°C).

【0049】

While the aforementioned process of cleaning the wafer W was described for the case where a mixed solution (SC1) of ammonia water, a hydrogen peroxide solution, and pure water is used as an the alkaline processing solution, the alkaline processing solution may be such that ozone water or the like be added as an oxidant in place of a hydrogen peroxide solution, or that a surface active agent be added. Using such an alkaline processing solution as containing an oxidant or a surface active agent brings about the effects of protecting the surface of the wafer W to be processed and inhibiting an increase in surface roughness. Still alternatively, dilute ammonia water may be used solely as an alkaline processing solution. For the sole use of dilute ammonia water, it is desirable that for the protection of the surface of the wafer W, the ratio of ammonia water (28 to 30 wt%; the same applies hereinafter) to pure water be in the range of 5:0.02 to 5:0.6 by volume. For the use of a mixed solution of ammonia water, a hydrogen peroxide solution, and pure water, it is desirable that for the maintenance of alkalinity, the ratio of pure water, ammonia water, and hydrogen peroxide solution (30 wt%; the same applies hereinafter) be in the range of 5:0.03:0.03 to 5:1:1 by volume.

【0050】

While the aforementioned process of cleaning the substrate W was described for the case where a mixed solution of hydrofluoric acid, hydrochloric acid, and pure water is used as an acid processing solution, the acid processing solution may contain dilute hydrochloric acid, dilute hydrofluoric acid, or dilute sulfuric acid. For the use of

dilute hydrochloric acid, it is desirable that the ratio of hydrochloric acid (35 wt%; the same applies hereinafter) to pure water be in the range of 1:3 to 1:15 by volume. For the use of a mixed solution of dilute hydrochloric acid, dilute hydrofluoric acid, and pure water, it is desirable that for suppression of the etching force with hydrofluoric acid, the ratio of hydrofluoric acid (50 wt%; the same applies hereinafter) to dilute hydrochloric acid be in the range of 1:50 to 1:500 by volume.

【0051】

The aforementioned process of cleaning the substrate W may include intermediate rinsing with pure water between step S2 and step S3 or between step S3 and step S4.

【0052】

While the wafer W is subjected in sequence to the droplet injection of the alkaline processing solution (step S2), the supply of the acid processing solution (step S3), and the droplet injection of the alkaline processing solution (step S4) in aforementioned cleaning procedure, for effective removal of particles including those that are difficult to remove, the droplet injection should be performed at least once simultaneously with or after slight surface etching of the wafer W with the acid processing solution. For effective and short-time removal of metal contaminants, on the other hand, the acid processing solution should be supplied to the wafer W after the supply of the alkaline processing solution. From this viewpoint, not only the aforementioned cleaning procedure but also other various cleaning procedures as shown in (a) to (d) of Fig. 6 allow effective and short-time removal of particles and metal contaminants, thereby achieving the object of the present invention. It is noted herein that Fig. 6 does not show any step (such as introduction and discharge of the wafer W, rinsing, and spin drying) other than the supply of the alkaline processing solution and the supply of the acid processing

solution. It is also noted that (a) to (d) of Fig. 6 are only illustrative examples and other various cleaning procedures may also be employed.

【0053】

In the cleaning procedure shown in (a) of Fig. 6, the wafer W is subjected in sequence to the supply of an alkaline processing solution (step SA1), the supply of an acid processing solution (step SA2), and the supply of the alkaline processing solution (step SA3); and both the supply of the alkaline processing solution (steps SA1 and SA3) and the supply of the acid processing solution (step SA2) are done by droplet injection. In order to implement this cleaning procedure, the apparatus shall be configured to employ a binary fluid nozzle in both the mechanism for supplying an alkaline processing solution and the mechanism for supplying an acid processing solution.

【0054】

In the cleaning procedure shown in (b) of Fig. 6, the wafer W is subjected in sequence to the supply of an alkaline processing solution (step SB1), the supply of an acid processing solution (step SB2), and the supply of the alkaline processing solution (step SB3); and out of those supplies, only the supply of the acid processing solution (step SB2) is a droplet injection. In order to implement this cleaning procedure, the apparatus shall be configured to employ an ordinary nozzle in the mechanism for supplying an alkaline processing solution and a binary fluid nozzle in the mechanism for supplying an acid processing solution.

【0055】

In the cleaning procedure shown in (c) of Fig. 6, the wafer W is subjected in sequence to the supply of an alkaline processing solution (step SC1) and the supply of an acid processing solution (step SC2); and out of those supplies, only the supply of an acid processing solution (step SC2) is a droplet injection. In order to implement this cleaning

procedure, the apparatus shall be configured to employ an ordinary nozzle in the mechanism for supplying an alkaline processing solution and a binary fluid nozzle in the mechanism for supplying an acid processing solution.

【0056】

In the cleaning procedure shown in (d) of Fig. 6, the wafer W is subjected to the supply of an alkaline processing solution (step SD1) and then to two repetitions of the supply of an acid processing solution and the following supply of the alkaline processing solution (steps SD2 to SD5); and out of those supplies, only the supply of an alkaline processing solution (steps SD1, SD3, and SD5) is a droplet injection. In order to implement this cleaning procedure, the apparatus shall be configured to employ a binary fluid nozzle in the mechanism for supplying an alkaline processing solution and an ordinary nozzle in the mechanism for supplying an acid processing solution. Alternatively, the apparatus configuration may includes a separate alkaline-processing-solution supply mechanism using an ordinary nozzle, in which part of the steps SD1, SD3, and SD5 may be the supply of an alkaline processing solution through the ordinary nozzle. The supply of an acid processing solution and the following supply of an alkaline processing in steps SD2 to SD5 may be repeated three or more times.

【0057】

It is however to be noted that the mode of supplying only either an alkaline or acid processing solution by a droplet injection is better than the mode of supplying both alkaline and acid processing solutions by a droplet injection, in preventing a number of droplets of the processing solution from floating in the atmosphere surrounding the wafer W being processed and thereby reducing the likelihood that those droplets will adhere to each part of the substrate processing apparatus and to the processed wafer W.

【0058】

In the steps of alternately supplying the alkaline processing solution and the acid processing solution, it is known that rinsing subsequent to the last supply of the alkaline processing solution is completed in a shorter time than rinsing subsequent to the last supply of the acid processing solution.

【0059】

While the aforementioned example was described for the case of using an external-mix binary fluid nozzle as shown in Fig. 4, an internal-mix binary fluid nozzle as shown in a longitudinal sectional view of Fig. 7 may be used. An internal-mix binary fluid nozzle 81 shown in Fig. 7 includes an air introduction tube 90 having a downwardly tapered through hole 92 in the axial center; a cylindrical liquid introduction cylinder 94 that is integrally fixed to the air introduction tube 90 to enclose the outer periphery thereof and that is integrally formed with a liquid introduction tube part 96 having a through hole 98 in the axial center; and a liquid-drop generation tube 100 having the upper part of a large diameter, the lower part in the shape of a straight tube of a small diameter, and the tapered middle part and having its upper end engaged and fixed to the lower part of the liquid introduction cylinder 94 to receive the lower end of the air introduction tube 90 with a gap. The lower part of the air introduction tube 90 is formed to have a small outer diameter, and there is an annular clearance between the lower outer peripheral surface of the air introduction tube 90 and the inner peripheral surface of the liquid introduction tube 94 to form an annular passage 102 that communicates with the through hole 98 in the liquid introduction tube part 96. There is also a clearance between the lower outer peripheral surface of the air introduction tube 90 and the upper inner peripheral surface of the liquid-drop generation tube 100 to form an annular discharge passage 104 that is channel-connected to the annular passage 102 and opens

into the liquid-drop generation tube 100. The lower end of the liquid-drop generation tube 100 forms an injection port 101.

【0060】

The through hole 92 in the air introduction tube 90 is openly connected with an air supply pipe 106 that is channel-connected to a compressed-air source (not shown). The air supply pipe 106 has an on-off control valve 108 inserted therein. The through hole 98 in the liquid introduction tube part 96, which is integrally formed with the liquid introduction cylinder 94, is openly connected with a liquid supply pipe 111 that supplies a liquid such as an alkaline processing solution or an acid processing solution. The liquid supply pipe 111 is channel-connected through an on-off control valve 116 to a liquid supply source (not shown).

【0061】

In the internal-mix binary fluid nozzle 81 described above, when the on-off control valve 116 is opened (at this time an on-off control valve 118 is in a closed position) to supply a liquid from the liquid supply source through the liquid supply pipe 111 to the liquid introduction tube part 96 of the liquid introduction cylinder 94, the liquid passes through the annular passage 102 and the annular discharge passage 104 and is then discharged obliquely downwardly from the lower-end opening of the annular discharge passage 104 into the axial center of liquid-drop generation tube 100. When the on-off control valve 108 is opened to supply compressed air from the compressed air source through the air supply pipe 106 to the air introduction tube 90, on the other hand, the compressed air is discharged from the lower-end discharge port of the air introduction tube 90 directly downwardly into the liquid-drop generation tube 100. Inside the liquid-drop generation tube 100, the compressed air collides with an etchant. This results in mixture of the liquid and the compressed air, generating droplets. The

rectilinear propagation property is imparted to droplets 120 generated in the liquid-drop generation tube 100 while they pass through a straight tube part formed in the small-diameter part of the liquid-droplet generation tube 100, so that the droplets 120, issuing directly downwardly from the lower-end injection port 101 of the liquid-drop generation tube 100, are injected onto the surface of the wafer W.

【0062】

However, like the internal-mix binary fluid nozzle 81, the previously-described external-mix binary fluid nozzle 48 has the advantage of not dropping a liquid from the nozzle tip when unnecessary. The external-mix binary fluid nozzle 48 also has the advantage of simplifying flow-pressure control as compared to the internal-mix binary fluid nozzle 81, because neither the flow pressure of gas nor the flow pressure of a liquid serves as resistance against the other.

【0063】

While the aforementioned example of the process of cleaning the wafer W is described for the case where the impact caused by the droplet injection is effectively used for physical particle removal without any damage to the wafer W, another embodiment of the present invention may take advantage of an impact caused by ultrasonic vibrations imparted to a processing solution. Fig. 8(a) is a perspective view of an ultrasonic nozzle 69 capable of imparting ultrasonic vibrations to a liquid such as a processing solution, and Fig. 8(b) is a longitudinal sectional view of the ultrasonic nozzle 69 including a pipe 37a. The ultrasonic nozzle shown in Fig. 8 includes a lidded cylindrical discharge part 69b, the lower half of which has a V-shaped section and which has a discharge port 69a formed in the lower end face; and an ultrasonic vibrator 69d fixed to one end of a through hole 69c formed in the upper wall surface of the discharge part 69b. The discharge part 69b is made of a material with chemical resistance, such as fluororesin. A thin plate of quartz

or high-purity SiC (silicon carbide) is bonded to the surface of the ultrasonic vibrator 69d. The ultrasonic vibrator 69d is electrically connected with a cable 67 that is electrically connected to a high-frequency oscillator not shown. The ultrasonic vibrator 69d is capable of emitting ultrasonic waves toward a liquid that fills up the discharge part 69b and imparting ultrasonic vibrations to a liquid discharged from the discharge pot 69a. The discharge part 69b has a liquid inlet 71 formed on the side wall surface, and the liquid inlet 71 is openly connected with a pipe 37a. The pipe 37a is openly connected with a liquid supply source (not shown). In other words, it is possible to supply a liquid through the pipe 37a into the discharge part 69b of the ultrasonic nozzle 69 and then to discharge the liquid, to which ultrasonic vibrations are imparted with the ultrasonic vibrator 69d, from the discharge port 69a onto the surface of the wafer W.

【0064】

Fig. 9 is a graph showing the result of a test for the removal rates of SiN and PSL (particles) in the process of cleaning the wafer W with the substrate processing apparatus described above. A mixed solution of ammonia water, a hydrogen peroxide solution, and pure water (the rate of ammonia water, a hydrogen peroxide solution, and pure water is 1:1:100 by volume) was used as the alkaline processing solution, and a mixed solution of dilute hydrofluoric acid and dilute hydrochloric acid (the rate of hydrofluoric acid, hydrochloric acid, and pure water is 1:40:200 by volume) was used as the acid processing solution. This test was conducted under the condition that the wafer W had a water-repellent surface so that particles were hard to remove.

【0065】

Under processing condition C1, after a 10-second injection of the alkaline processing solution as droplets onto the surface of the wafer W, the acid processing solution was supplied to the surface of the wafer W for 10 seconds, and then, the alkaline

processing solution as droplets was again injected onto the surface of the wafer W for 10 seconds.

【0066】

Under processing condition C2, a 10-second injection of the alkaline processing solution as droplets to the surface of the wafer was repeated twice.

【0067】

Under processing condition C3, after a 10-second injection of the alkaline processing solution as droplets to the surface of the wafer W, the acid processing solution was supplied to the surface of the wafer W for 10 seconds.

【0068】

According to the result in Fig. 9, the particle removal rates under processing condition C1 are superior to those under processing conditions C2 and C3. That is, the result shows that a droplet injection of the alkaline processing solution after processing with the acid processing solution yields a high particle removal rate.

【Brief Description of the Drawings】

【0048】

【Fig. 1】 is a plan view showing, by way of example, a structure of the substrate processing apparatus according to the present invention;

【Fig. 2】 is a schematic end view of the essential parts of the substrate processing apparatus when viewed from the direction of the arrow A in Fig. 1;

【Fig. 3】 is a schematic end view of the essential parts of the substrate processing apparatus when viewed from the direction of the arrow B in Fig. 1;

【Fig. 4】 is a longitudinal sectional view showing, by way of example, a structure of a binary fluid nozzle in the substrate processing apparatus shown in Fig. 1;

【Fig. 5】 shows, by way of example, the steps in the process of cleaning the

wafer W according to the present invention;

【Fig. 6】 illustrates various cleaning procedures according to the present invention;

【Fig. 7】 is a longitudinal sectional view showing, by way of example, a structure of an internal-mix binary fluid nozzle;

【Fig. 8】 shows a perspective view of the ultrasonic nozzle 69 and a longitudinal sectional view of the ultrasonic nozzle 69 including the pipe 37a; and

【Fig. 9】 is a graph showing the results of a test for the rates of SiN and PSL (particle) removal in the process of cleaning the wafer W.

【Explanation of Referenced Numerals】

【0070】

46: a mechanism for supplying an alkaline processing solution;

48: a binary fluid nozzle;

69: an ultrasonic nozzle;

78: a mechanism for supplying an acid processing solution;

80: a nozzle;

81: an internal-mix binary fluid nozzle;

91: a control part;

W: a wafer

【Document Name】 Abstract

【Abstract】

【Problems to be Solved】 A substrate processing technique is provided which allows effective and short-time removal of particles and metal contaminants from a substrate surface without any increase in the amount of etching of the substrate surface.

【Means to Solve the Problems】 A wafer is subjected in sequence to an injection of droplets of an alkaline processing solution (step S2); a supply of an acid processing solution (step S3); and an injection of droplets of the alkaline processing solution (step S4). Particles adhering to the wafer surface are removed effectively in a short time by the combined use of etching of the substrate surface with the acid processing solution and physical action of the droplet injection or ultrasonic vibrations. Metal contaminants adhering to the wafer surface are removed effectively in a short time because they are dissolved in the acid processing solution after converted into hydroxides with the alkaline processing solution. It is thus possible to minimize the amount of etching of the substrate surface, unlike in the case where particles and metal contaminants are removed mainly by etching of the substrate surface.

【Selected Figure】 Fig. 5

FIG. 1

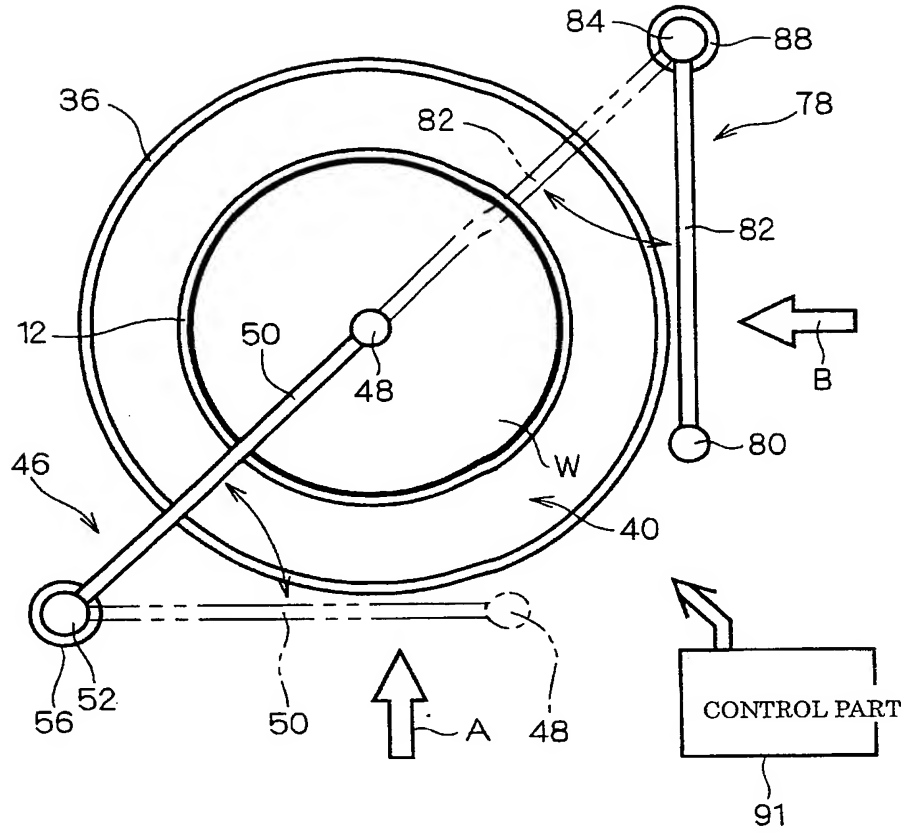


FIG. 2

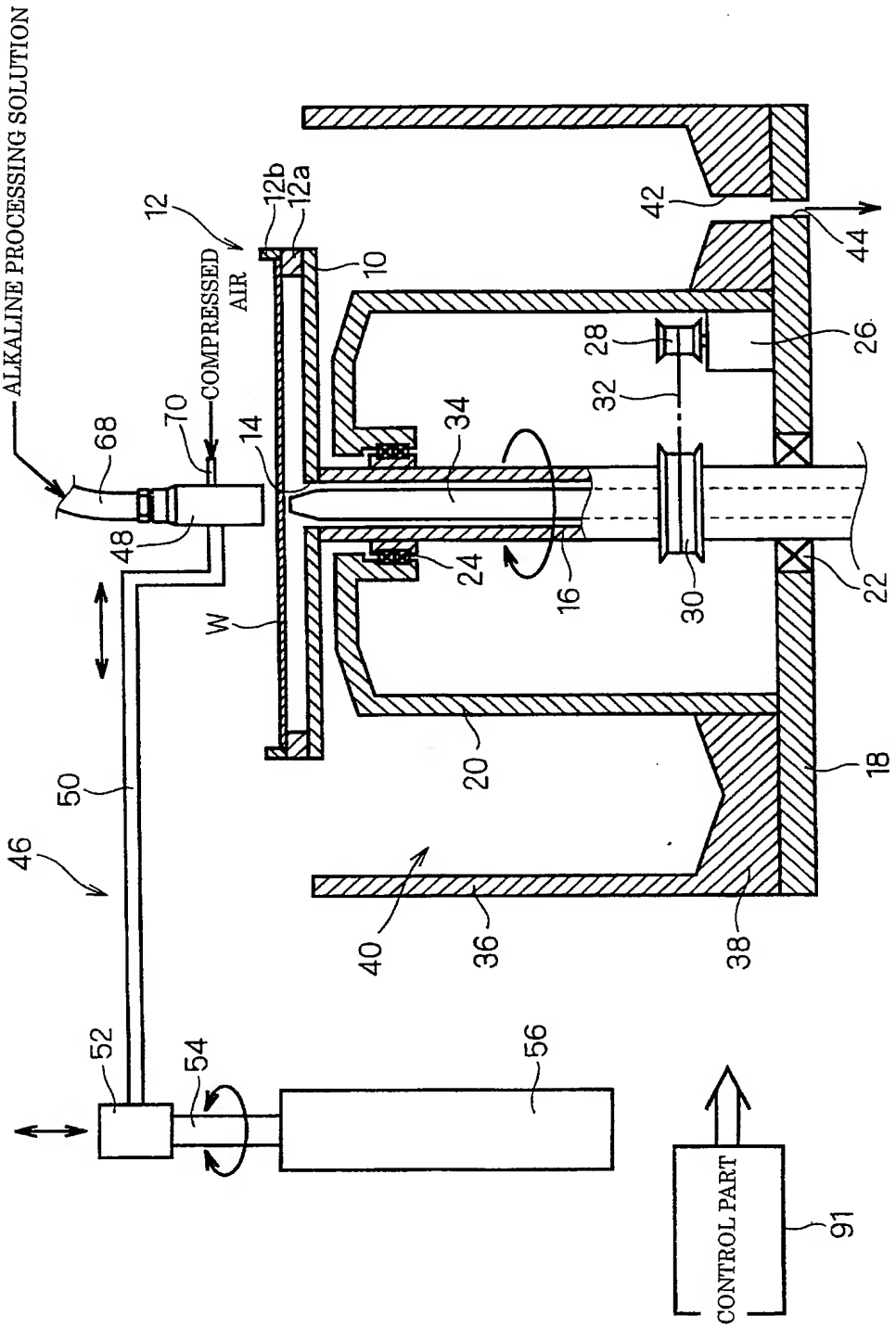

ALKALINE PROCESSING SOLUTION
COMPRESSED AIR
CONTROL PART
12
12b
12a
10
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
68
70
91
W

FIG. 3

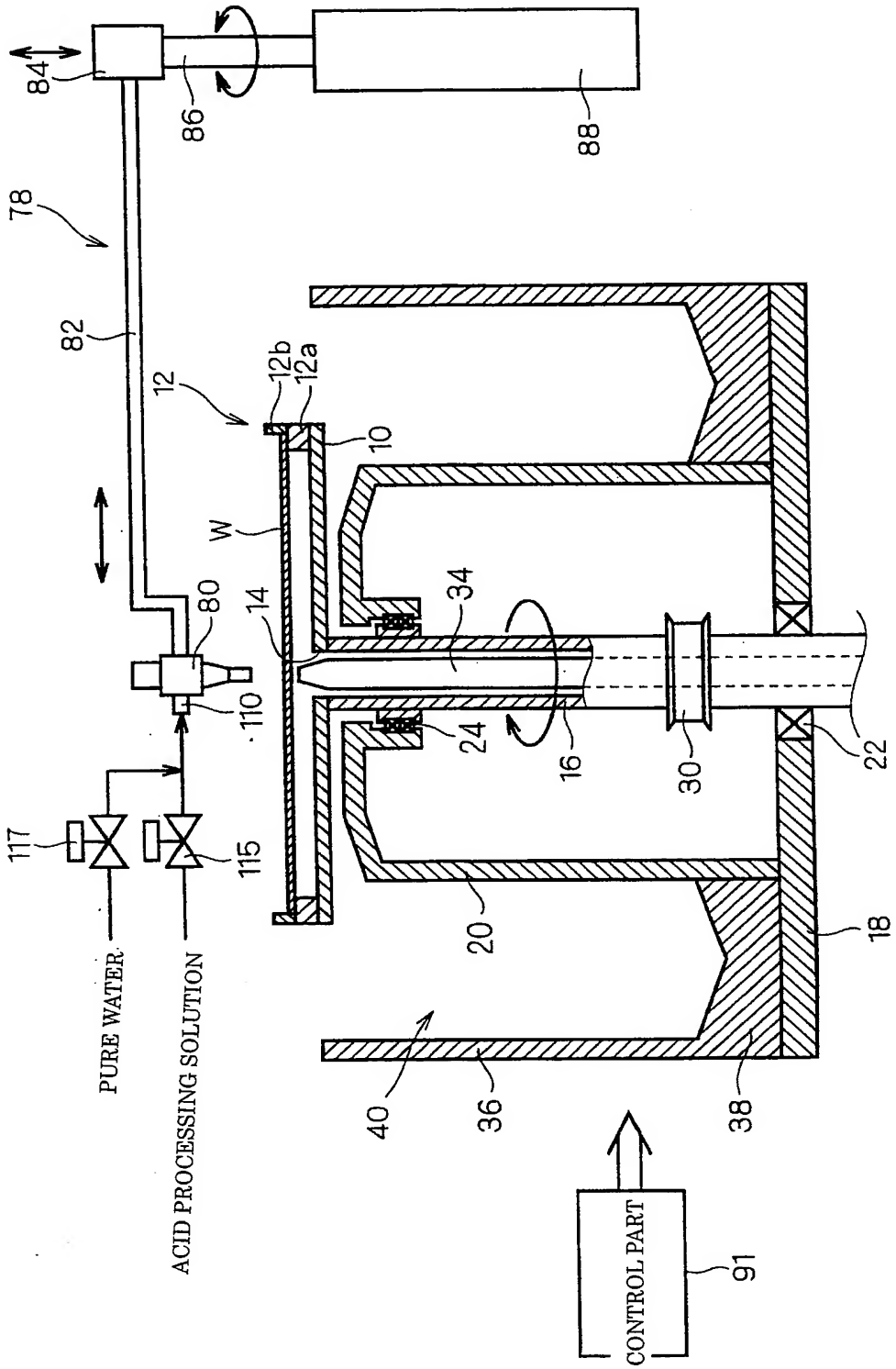

84
86
88
78
82
12
12b
12a
10
W
80
14
34
110
24
16
30
22
117
115
20
18
PURE WATER
ACID PROCESSING SOLUTION
40
36
38
CONTROL PART
91

FIG. 4

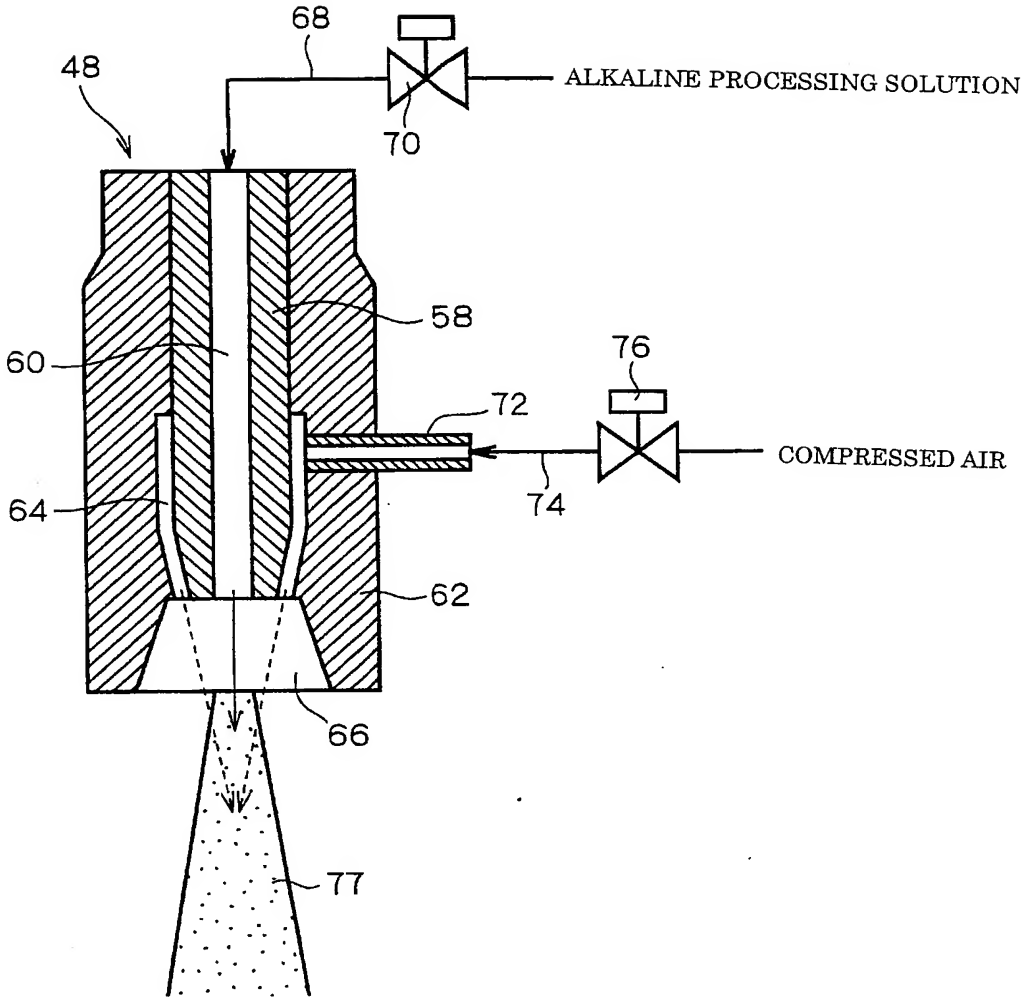

68
48
ALKALINE PROCESSING SOLUTION
70
58
60
76
72
COMPRESSED AIR
74
64
62
66
77

FIG. 5

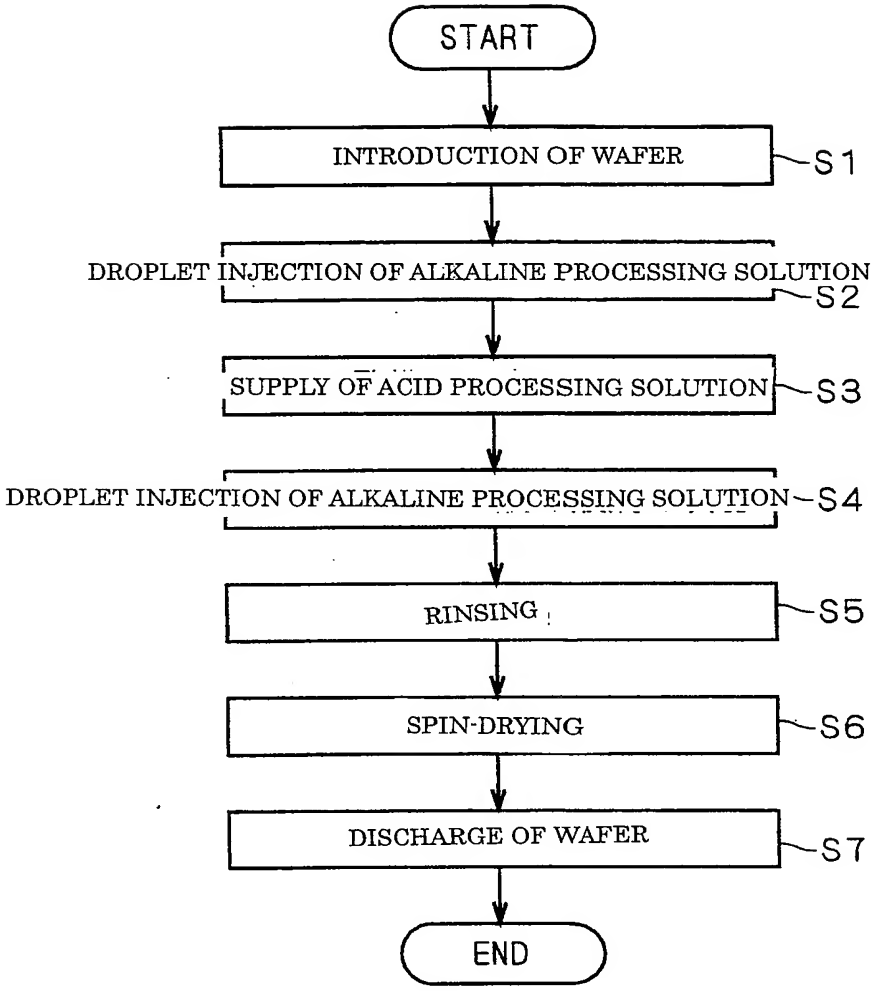

START
INTRODUCTION OF WAFER
S1
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
S2
SUPPLY OF ACID PROCESSING SOLUTION
S3
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
S4
RINSING
S5
SPIN-DRYING
S6
DISCHARGE OF WAFER
S7
END

FIG. 6

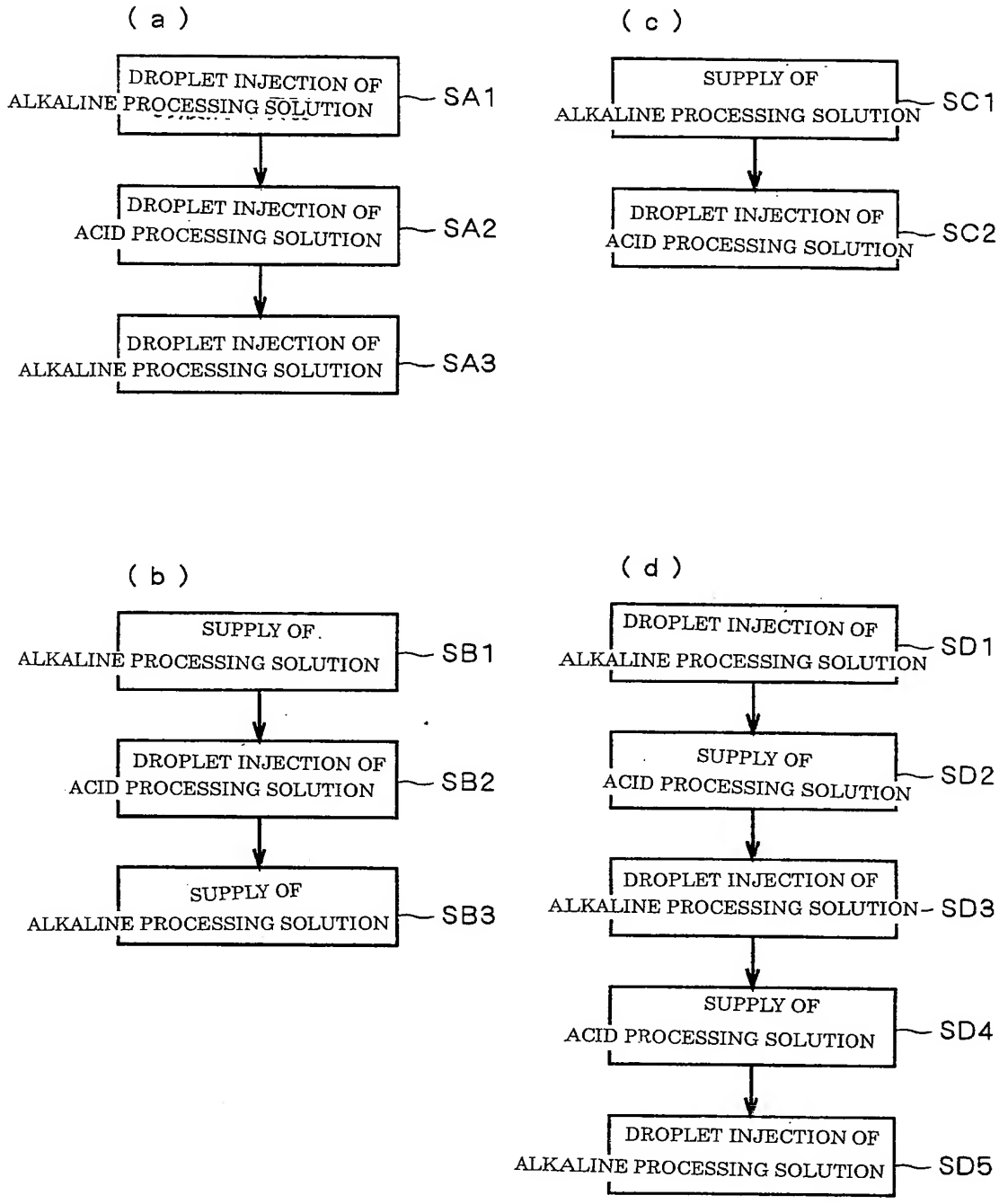

(a)
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
SA1
DROPLET INJECTION OF ACID PROCESSING SOLUTION
SA2
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
SA3
(c)
SUPPLY OF ALKALINE PROCESSING SOLUTION
SC1
DROPLET INJECTION OF ACID PROCESSING SOLUTION
SC2
(b)
SUPPLY OF ALKALINE PROCESSING SOLUTION
SB1
DROPLET INJECTION OF ACID PROCESSING SOLUTION
SB2
SUPPLY OF ALKALINE PROCESSING SOLUTION
SB3
(d)
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
SD1
SUPPLY OF ACID PROCESSING SOLUTION
SD2
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
SD3
SUPPLY OF ACID PROCESSING SOLUTION
SD4
DROPLET INJECTION OF ALKALINE PROCESSING SOLUTION
SD5

FIG. 7

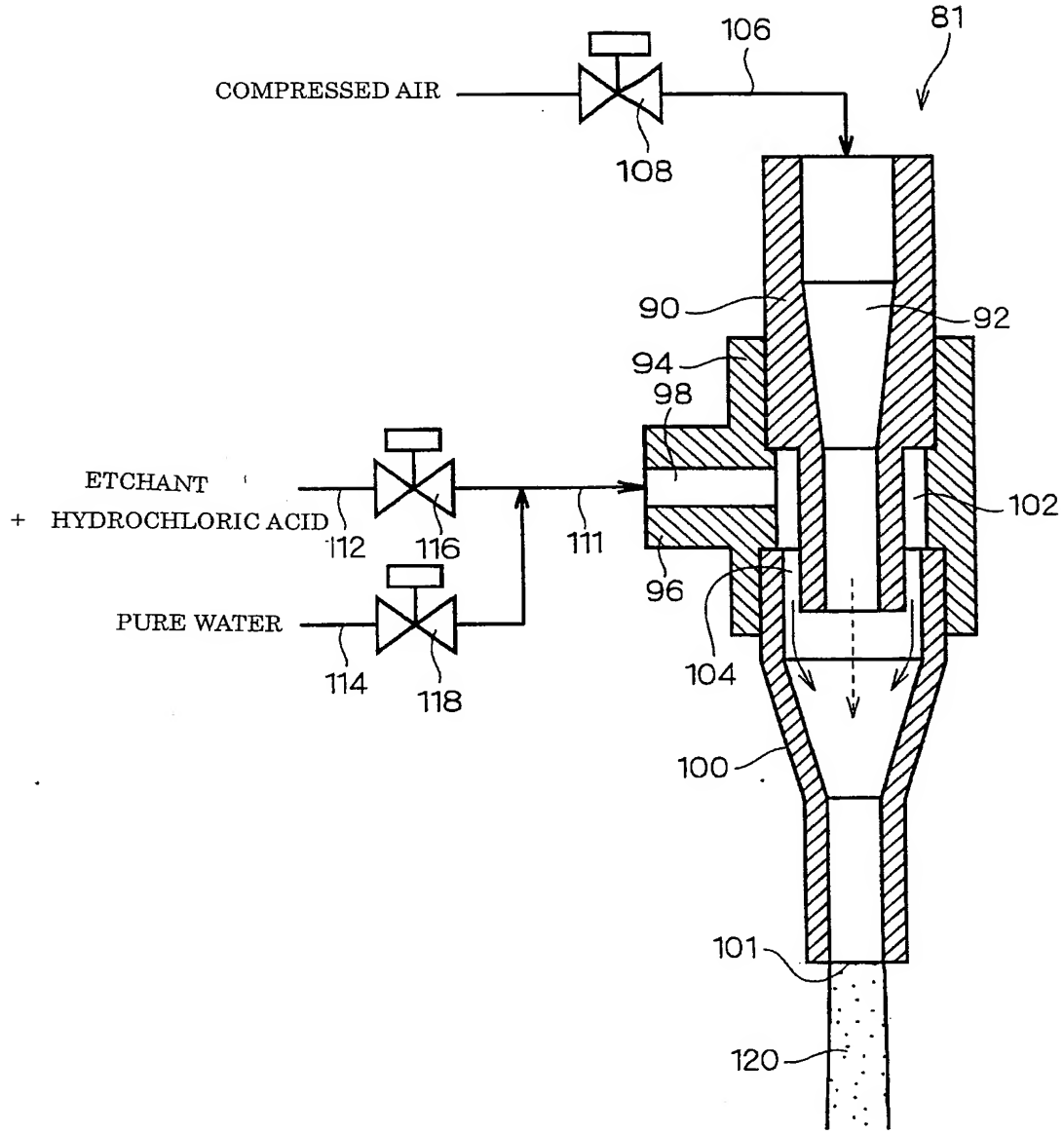
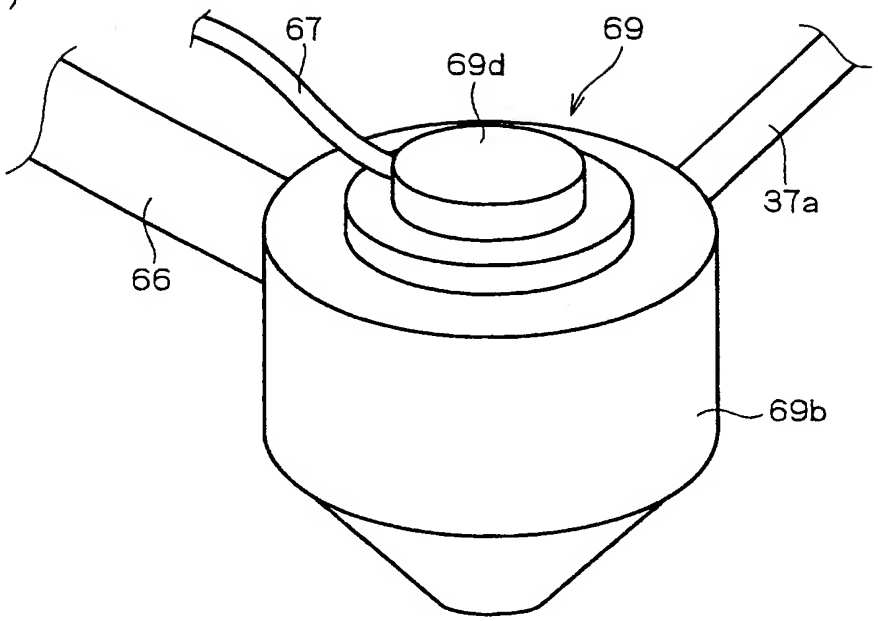

COMPRESSED AIR
106
81
108
90
92
94
98
ETCHANT
+ HYDROCHLORIC ACID
112
116
111
102
96
PURE WATER
114
118
104
100
101
120

FIG. 8

(a)



(b)

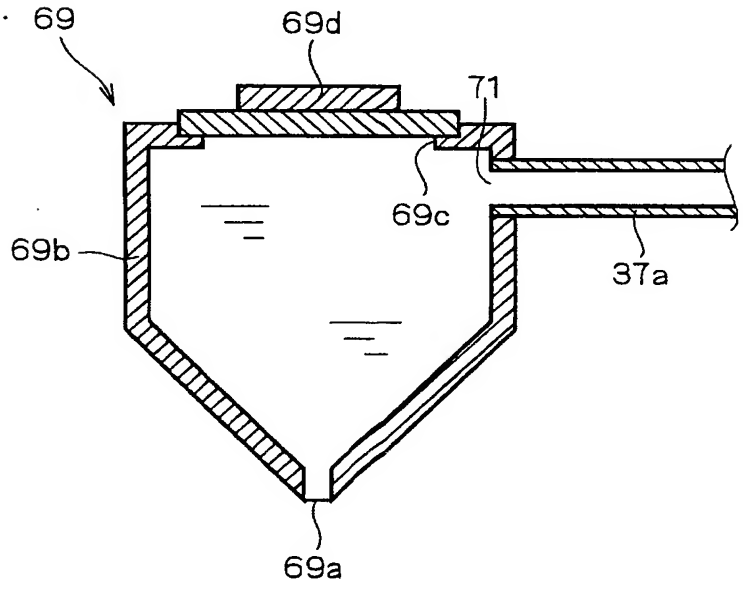


FIG. 9